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(21) International Application Number: PCT/US97/08140 (22) International Filing Date: 12 May 1997 (12.05.97) (30) Priority Data: 96107909.2 17 May 1996 (17.05.96) EP (34) Countries for which the regional or international application was filed: DE et al. (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors: AUDENAERT, Frans, A.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). ALLEWAERT, Kathy, E., M., L., A.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). HOOFTMAN, Gert; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). NAGASE, Makoto; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). LENS, Hugo, R.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: MAKI, Eloise, J. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: FLUORO-CHEMICAL POLYURETHANES, PROVIDING GOOD LAUNDRY AIR-DRY PERFORMANCE (57) Abstract The present invention relates to fluorochemical polyurethane compounds of formula (I) according to claim 1, a method for their preparation and to compositions comprising that fluorochemical polyurethane compound. The compound and the composition comprising that compound are suitable to impart durable oil- and water-repellency and good laundry air-dry performance to substrates, such as fibers, woven or non-woven fabrics, carpets, leather and paper.		

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FLUOROCHEMICAL POLYURETHANES, PROVIDING GOOD LAUNDRY AIR-DRY PERFORMANCE

This invention relates to oil- and water-repellent fluorochemical compositions comprising fluorochemical polyurethanes derived from functionalized fluorochemical oligomers and isocyanates. This invention, in another aspect, relates to a method for imparting oil- and water-repellent properties to fibrous substrates and other materials and to the resulting treated substrates.

The use of various fluorochemical compositions on fibers and fibrous substrates, such as textiles, paper and leather, to impart oil- and water-repellency is known. See for example, Banks, Ed., Organofluorine Chemicals and Their Industrial Applications, Ellis Horwood Ltd., Chichester, England, 1979, pp. 226-234.

Certain fluorinated compounds containing urethane bonds are known. A common synthetic route for forming such compounds containing urethane bonds uses isocyanate compounds as starting materials. The use of blocking or masking agents to 'protect' the unreacted isocyanate moieties is also known.

U.S. Patent No. 3,398,182 teaches fluorocarbon compounds which contain a highly fluorinated oleophobic and hydrophobic terminal portion and a different nonfluorinated oleophilic portion linked together by a urethane radical obtained by reacting together an isocyanate and a highly fluorinated organic compound containing an active hydrogen. Surfaces coated with such fluorocarbon compounds are oleophobic and hydrophobic and the coating is durable, resisting removal by abrasion.

U.S. Patent No. 4,788,287 and U.S. Patent No. 4,792,354 disclose a water and oil repellent compound having at least two terminal segments and an intermediate segment connecting the terminal segments and having a molecular weight of from 800 to 20,000, each terminal segment containing at least one polyfluoroalkyl group connected by a -CONH-linking group, the intermediate segment being a urethane oligomer containing at least two -CONH- linking groups

in one molecule, and said terminal segments and intermediate segment being connected by a -CONH- linking group. The urethane oligomer of U.S. Patent No. 4,792,354 further contains a hydrophilic molecular chain.

U.S. Patent Nos. 5,276,175 and 5,453,540 teach fluorochemical compositions comprising fluorinated compounds, wherein the fluorinated compound comprises a fluorochemical oligomeric portion, an organic moiety, and a group that can impart soft hand, stain release, water repellency, or a durable property when the compound is applied to a fibrous substrate, wherein the fluorochemical oligomeric portion is bonded to the organic moiety through an isocyanate-derived linking group.

U.S. Patent Nos. 5,276,175 and 5,453,540 disclose fluorochemical compositions comprising fluorinated compounds, wherein the fluorinated compound comprises a fluorochemical oligomeric portion, an organic moiety, and a group that can impart soft hand, stain release, water-repellency, or a durable property when the compound is applied to a fibrous substrate, wherein the fluorochemical oligomeric portion is bonded to the organic moieties through an isocyanate-derived linking group. These fluorochemical compounds, however, are not polyurethanes in the sense of the present invention, because the patents teach that, if a reagent containing two or more functional groups reactive to an isocyanate is used to prepare the compound, at least one of the functional groups will have a substantially lesser degree of reactivity with isocyanates than the others and the less reactive group will generally remain unreacted; see U.S. Patent No. 5,276,175, column 22, lines 27-35, and U.S. Patent No. 5,453,540, column 20, lines 58-66.

U.S. Patent No. 5,491,261 discloses di-, tri- and poly-perfluoroalkyl-substituted alcohols and acids and derivatives thereof which are prepared from perfluoroalkyl iodides and di-, tri- or polyallyl alcohols or acids. They can be reacted with isocyanates, epoxy compounds, anhydrides, acids or acid derivatives to prepare a great variety of oil- and water-repellent compositions.

The inclusion of silicone moieties in treatments with fluorochemicals which provide oil- and water-repellency is known to improve the feel or 'hand' of the treated substrates.

U.S. Patent No. 5,260,400 relates to silicone and perfluoroalkyl group containing telomers useful as coatings on glass, paper, wood, leather and especially textiles.

U.S. Patent No. 4,098,742 teaches polyurethanes which contain at least one segment derived from a perfluoroalkyl-substituted diol and at least one segment derived from a reactive-hydrogen-containing polysiloxane, which are synthesized by co-polycondensation with an organic diisocyanate.

U.S. Patent No. 5,258,458 discloses a composition for treating fibrous substrates such as textiles to provide oil and water repellency. The composition comprises a) a terpolymer comprising randomly distributed i) units containing a fluoroaliphatic group, Rf, ii) fluorine-free hydrocarbon units, and iii) units containing silicone and b) a fluorine-containing polymer having isocyanate derived linking groups and blocked isocyanate moieties.

European Patent Publication 0 383 310 A2 teaches a water and oil repellent containing a copolymer of a first vinyl monomer having a perfluoroalkyl group, a second vinyl monomer having a polyorganosiloxane chain and a third vinyl monomer having an isocyanate group or blocked isocyanate group as essential components. As an alternative, a water and oil repellent contains a copolymer of a first vinyl monomer having a polyorganosiloxane chain and a second vinyl monomer having an isocyanate group or blocked isocyanate group, in combination with a water and oil repellent compound having a perfluoroalkyl group.

U.S. Patent No. 5,019,428 teaches that modified polyurethanes containing perfluoroaliphatic groups which are obtained by reacting oligo(poly)urethanes containing free hydroxyl or isocyanate groups and perfluoroaliphatic groups with di/polyfunctional polysiloxanes at elevated temperatures with conversion of all the reactive groups of the urethane are used for the oil- and water-repellent finishing of fiber materials.

Environmental and safety concerns nowadays require the majority of all repellent treatment applications to be made from aqueous formulations in place of organic solvents. Practically all of the known compositions which can be applied from an aqueous emulsion require a heat-curing step after application and drying.

U.S. Patent No. 5,344,903 teaches that lower homologue perfluoroalkylethyl (meth)acrylates copolymerized with vinylidene chloride and alkyl (meth)acrylates; optionally with N-methylolacrylamide, hydroxyalkyl (meth)acrylates, and/or alkyloxy(meth)acrylates impart high levels of water-, alcohol- and oil-repellency to fabrics under mild conditions.

U.S. Patent No. 5,350,795 discloses fluorochemical compositions for treating textile fibers and fabrics to impart oil and water repellency without thermal treatment. The compositions comprise an aqueous, substantially organic solvent free, solution or dispersion of (a) a fluorochemical acrylate copolymer comprised of a fluorinated acrylate monomer, polyalkylene glycol acrylate or methacrylate, and polyalkylene glycol diacrylate or dimethacrylate; and (b) a polyalkoxylated polyurethane having pendant perfluoroalkyl groups comprised of an aliphatic or aromatic tri- or higher order isocyanate, a fluorinated alcohol, amine or mercaptan, and a poly(oxyalkylene)diol or dithiol.

Although water- and oil-repellent treating agents are readily available, it is very difficult to combine high initial oil- and water-repellency with excellent laundering and dry-clean durability. Furthermore, many high performance fluorochemicals have a tendency to impart a harsh feeling to the treated fabric. Although silicones can be applied to overcome this problem, silicones are usually not compatible with the fluorochemicals and therefore, the treated substrates typically will show a decrease in water and especially oil repellency.

Although existing patents claim durable repellent compositions, resistant to laundering and dry cleaning, they virtually all require a heat treatment after home launderings in order to regain the repellent properties. In known textile treatments, especially the dynamic water repellency is completely lost without heat treatment.

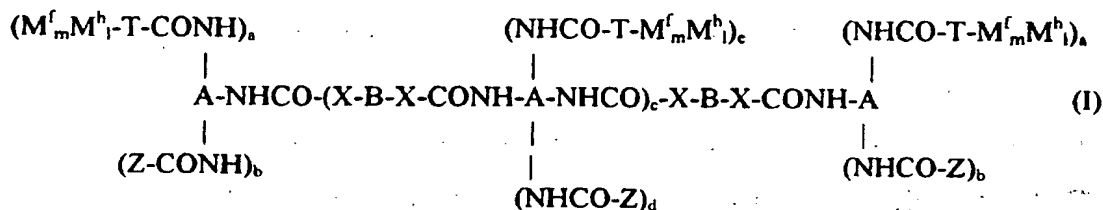
The present invention provides fluorochemical polyurethane compounds exhibiting high initial and durable oil- and water-repellent properties. It also provides a method of preparing such fluorochemical polyurethane compounds. It further provides a composition comprising a fluorochemical polyurethane compound which is suitable to impart durable oil- and water-repellency to a substrate treated therewith. The composition of the present invention should

furthermore provide good laundry air-dry performance, i.e., durable repellent properties after home launderings without a heat treatment step required. In addition, the composition of the present invention should be curable at low temperatures.

The fluorochemical polyurethane compound useful in this invention can be prepared by reacting:

- (a) a fluorochemical oligomer comprising the oligomerization product of fluorochemical monomers alone or in combination with fluorine-free monomers, in the presence of at least one functionalized chain transfer agent
- (b) a di-, tri-, or tetravalent isocyanate or combinations thereof,
- (c) at least one difunctional chain extender, and
- (d) at least one blocking or masking group.

A first subject-matter of the present invention is thus a fluorochemical polyurethane compound represented by formula (I)



wherein:

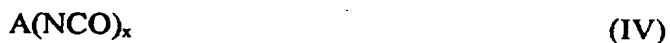
- $M_m^f M_l^h$ is a fluorochemical oligomer, comprising m units derived from a fluorochemical monomer and l units derived from a fluorine-free monomer, wherein the fluorochemical monomers and the fluorine-free monomers may be the same or different;
- m is a number from 2 to 40, inclusive;
- l is a number from 0 to 20, inclusive;
- T is an organic linking group obtained by removing a hydrogen atom from a chain transfer agent, and the residues T may be the same or may be different;
- Z is the residue obtained by removing a hydrogen atom from an organic masking or blocking group, and the residues Z may be the same or may be different;

- A is a di- tri- or tetravalent residue obtained by removing 2, 3 or 4 -NCO groups from a corresponding isocyanate, and the residues A may be the same or may be different;
- B is a divalent organic residue obtained by removing the two X-H groups from a difunctional active hydrogen compound HX-B-XH, wherein X is O, NH or S, and the residues B may be the same or may be different;
- a is a number from 1 to 3, inclusive and b is a number from 0 to 2, inclusive, with the proviso that a+b has a value from 1 to 3;
- c is a number from 0 to 30 inclusive;
- d and e are numbers from 0 to 2, inclusive, provided that d+e is not greater than 2.

Another subject-matter of the present invention is a method of preparing a fluorochemical polyurethane compound of formula (I) which comprises reacting a fluorochemical oligomer of the formula (III)



wherein $M_m^f M_n^h$ and T are defined as above, with at least one isocyanate of formula (IV)



wherein A is defined as above and x is a number from 2 to 4, inclusive, at least one bifunctional active hydrogen compound of formula (V)



wherein X and B are defined as above, and at least one compound of formula (VI)



wherein Z is defined as above.

The fluorochemical polyurethane compound may be used in the form of a solution or dispersion and is generally employed as a composition comprising the said compound which composition constitutes a further subject-matter of the invention. The treatment provides strong initial repellency to substrates including textile fibers, such as cotton, polyester, polyamide or blends thereof, protective clothing made from aramid type fibers or polyvinyl chloride, fabrics such as apparel, upholstery and carpet, non-wovens, leather, paper, wood, metal, glass, concrete and

stone, and displays a high durability to dry cleaning and home laundering. Even when treatment was carried out at low cure conditions, the treatment composition using the fluorochemical polyurethane compound of the present invention provides especially good oil- and water-repellency after multiple launderings even without heating the substrate after laundering. This special feature will be further referred to as laundry air-dry (LAD) effect or performance. It is also possible to include segments, e.g., polysiloxane segments, into the fluorochemical polyurethane compound of the present invention which in addition to durable oil- and water-repellency impart a gentle touch to the treated substrates.

Still another subject matter of the present invention is the use of a fluorochemical polyurethane compound or of a composition comprising said compound to impart durable oil- and water-repellency and good laundry air-dry performance to a substrate treated therewith. Said treatment comprises the steps of (1) applying to the surface of a substrate an amount of the fluorochemical polyurethane compound of the invention or of a composition comprising said compound, effective to impart oil- and water-repellent properties to the substrate, wherein said compound is present in an amount of 0.01% to 5% by weight based on the weight of the substrate, and (2) heating the treated substrate from step 1 at a temperature and for a time sufficient to cure the treated substrate.

The compounds of the present invention represented by the formula (I) are polyurethanes, i.e., they comprise at least one polymeric portion within their molecule which is obtained by the reaction of isocyanate groups containing compounds with a chain extender having two isocyanate reactive X-H groups. The moiety derived from the chain extender is represented in the formula (I) by the residue -X-B-X-. These fluorochemical polyurethane compounds exhibit the surprising ability to impart not only high initial oil- and water-repellency to treated substrates but also durable repellency which does not disappear after repeated launderings and -- what is most surprising -- good laundry air-dry performance which means that it is not necessary to heat, e.g., iron, the substrate after laundering to reestablish repellency. Drying of the substrate in the air is sufficient to regenerate good oil- and water-repellent properties.

The fluorochemical polyurethane compounds of the present invention exhibit superior laundry air-dry characteristics as compared with the compositions disclosed in U.S. Patent Nos. 5,276,175 and 5,453,540.

The fluorochemical polyurethane compounds of the present invention can be prepared in a two step reaction. In a first step, a functionalized fluorochemical oligomer is prepared, which in a second step is further reacted to form a polyurethane.

In a first step, a fluorochemical oligomer is conveniently prepared by free-radical oligomerization of fluorochemical monomers (R_f -Q-D) alone or in combination with hydrocarbon monomers (R_h -D'), in the presence of hydroxy-, amino-, or mercapto functionalized chain transfer agents. The aliphatic backbone of the fluorochemical oligomeric portion comprises a sufficient number of polymerized units to render the portion oligomeric. The aliphatic backbone preferably comprises from 2 to about 40 polymerized units derived from fluorochemical monomers and from 0 to about 20 polymerized units derived from hydrocarbon monomers.

The fluoroaliphatic radical, R_f , in the fluorochemical monomer, is a fluorinated, stable, inert, preferably saturated, non-polar, monovalent aliphatic radical. It can be straight chain, branched chain, or cyclic or combinations thereof. It can contain heteroatoms such as oxygen, divalent or hexavalent sulfur, or nitrogen. R_f is preferably a fully-fluorinated radical, but hydrogen or chlorine atoms can be present as substituents if not more than one atom of either is present for every two carbon atoms. The R_f radical has at least 3 and up to 18 carbon atoms, preferably 3 to 14, especially 6 to 12 carbon atoms, and preferably contains about 40% to about 80% fluorine by weight, more preferably about 50% to about 78% fluorine by weight. The terminal portion of the R_f radical is a perfluorinated moiety, which will preferably contain at least 7 fluorine atoms, e.g., $CF_3CF_2CF_2-$, $(CF_3)_2CF-$, F_3SCF_2- . The preferred R_f radicals are fully or substantially fluorinated and are preferably those perfluorinated aliphatic radicals of the formula $C_nF_{2n+1}-$ where n is 3 to 18.

The linking group Q links the fluoroaliphatic group R_f to the ethylenically unsaturated alkylene segment D. Linking group Q preferably contains from 1 to

about 20 carbon atoms. Q can optionally contain oxygen, nitrogen, or sulfur-containing groups or a combination thereof, and Q is preferably free of functional groups that substantially interfere with free-radical oligomerization (e.g., polymerizable olefinic double bonds, thiols, easily abstracted hydrogen atoms such as cumyl hydrogens, and other such functionality known to those skilled in the art). Examples of suitable linking groups Q include straight chain, branched chain or cyclic alkylene, arylene, aralkylene, oxy, oxo, hydroxy, thio, sulfonyl, sulfoxo, amino, imino, sulfonamido, carboxyamido, carbonyloxy, urethanylene, ureylene, and combinations thereof such as sulfonamidoalkylene. Preferred linking groups

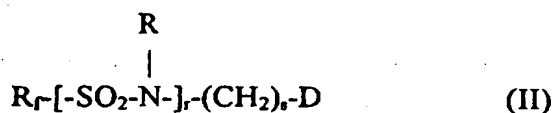
R
|

comprise groups of the formula $[-SO_2-N-]_r-(CH_2)_s-$ wherein R is methyl or ethyl; r is 0 or 1 and s is 1 to 8, preferably 1 or 2. Especially preferred linking groups include $-(CH_2CH_2)_k-$ and $-SO_2N(R)CH_2CH_2-$ wherein k is 1 or 2 and R is defined as above.

R_h is a fluorine-free organic group.

D and D' contain an ethylenically unsaturated segment capable of copolymerization with itself or each other. Suitable segments include, for example, moieties derived from vinyl ethers, vinyl esters, allyl esters, vinyl ketones, styrene, vinyl amide, acrylamides, maleates, fumarates, acrylates and methacrylates. Of these, the esters of alpha,beta unsaturated acids, such as the acrylates and methacrylates are preferred.

One particularly preferred fluorochemical monomer for use in the present invention can be represented by the following formula, wherein the fluorochemical oligomer is derived from a fluorochemical monomer of the formula (II):



wherein R_f is C_nF_{2n+1} with n being 3 to 18, preferably 6 to 12;

r is 0 or 1;

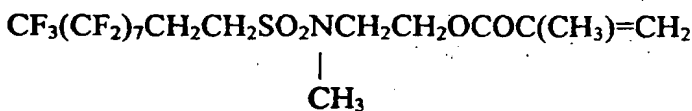
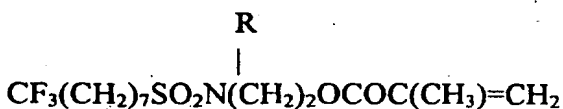
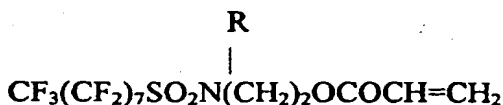
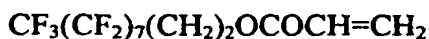
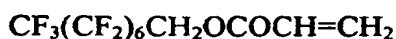
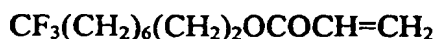
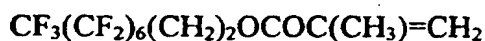
s is 1 to 8, preferably 1 or 2;

D is a group comprising a radically polymerizable unsaturated residue; and

R is methyl or ethyl.

Fluorochemical monomers R_f-Q-D as described above and methods for the preparation thereof are known and disclosed, e.g., in U.S. Patent No. 2,803,615. Examples of such compounds include general classes of fluorochemical acrylates, methacrylates, vinyl ethers, and allyl compounds containing fluorinated sulfonamido groups, acrylates or methacrylates derived from fluorochemical telomer alcohols, acrylates or methacrylates derived from fluorochemical carboxylic acids, and perfluoroalkyl acrylates or methacrylates as disclosed in EP-A-526 976.

Preferred examples of fluorochemical monomers include:



R = methyl or ethyl.

Hydrocarbon monomers R_h-D' suitable for the preparation of the fluorochemical oligomers are also well known and generally commercially available. Examples of such compounds include general classes of ethylenic compounds capable of free-radical polymerization, such as, for example, allyl esters such as allyl acetate and allyl heptanoate; alkyl vinyl ethers or alkyl allyl ethers such as cetyl vinyl ether, dodecylvinyl ether, 2-chloroethylvinyl ether, ethylvinyl ether; unsaturated

acids such as acrylic acid, methacrylic acid, alpha-chloro acrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid and their anhydrides and their esters such as vinyl, allyl, methyl, butyl, isobutyl, hexyl, heptyl, 2-ethyl-hexyl, cyclohexyl, lauryl, stearyl, isobornyl or alkoxy ethyl acrylates and methacrylates; alpha-beta unsaturated nitriles such as acrylonitrile, methacrylonitrile, 2-chloroacrylonitrile, 2-cyanoethyl acrylate, alkyl cyanoacrylates; alpha,beta-unsaturated carboxylic acid derivatives such as allyl alcohol, allyl glycolate, acrylamide, methacrylamide, n-diisopropyl acrylamide, diacetoneacrylamide, N,N-diethylaminoethylmethacrylate, N-t-butylamino ethyl methacrylate; styrene and its derivatives such as vinyltoluene, alpha-methylstyrene, alpha-cyanomethyl styrene; lower olefinic hydrocarbons which can contain halogen such as ethylene, propylene, isobutene, 3-chloro-1-isobutene, butadiene, isoprene, chloro and dichlorobutadiene and 2,5-dimethyl-1,5-hexadiene, and allyl or vinyl halides such as vinyl and vinylidene chloride. Preferred co-monomers which can be copolymerized with the above-described fluoroaliphatic radical-containing monomers include those selected from octadecylmethacrylate, 1,4-butanediol diacrylate, laurylmethacrylate, butylacrylate, N-methylol acrylamide, isobutylmethacrylate, ethylhexyl acrylate, ethylhexyl methacrylate, vinylchloride and vinylidene chloride.

The hydroxy-, amino and/or mercapto functionalized chain transfer agents T-H useful in the preparation of the fluorochemical oligomer include those selected from 2-mercaptoethanol, 3-mercapto-2-butanol, 3-mercapto-2-propanol, 3-mercapto-1-propanol, 3-mercapto-1,2-propanediol, 2,3-dimercaptopropanol, 2-mercapto-ethylamine and 2-mercaptoethylsulfide. A single compound or a mixture of different chain transfer agents may be used. The chain transfer agents which are preferably used in the preparation of the fluorochemical oligomer contain only two functional groups so that after reaction with the oligomer only one isocyanate reactive group remains on the obtained fluorochemical oligomer. The preferred chain transfer agent is 2-mercaptoethanol.

In order to prepare the functionalized fluorochemical oligomer, a free-radical initiator is present. Such free-radical initiators are known in the art and include azo compounds, such as azobisisobutyronitrile (AIBN) and azo-2-

cynovaleric acid and the like, hydroperoxides such as cumene, t-butyl, and t-amyl hydroperoxide, dialkyl peroxides such as di-t-butyl and dicumylperoxide, peroxyesters such as t-butylperbenzoate and di-t-butylperoxy phthalate, diacylperoxides such as benzoyl peroxide and lauroyl peroxide.

In a second step of the reaction, the fluorochemical oligomer is reacted with an isocyanate, a chain extender and a blocking or masking agent. Suitable isocyanates $A(NCO)_x$ with x being 2, 3 or 4, for use in preparing the fluorochemical polyurethanes of formula I include aromatic diisocyanates such as 4,4'-methylene-diphenylene diisocyanate (MDI) and 2,4-toluene diisocyanate (2,4-TDI); alicyclic diisocyanates such as 3-isocyanatomethyl-3,5,5-trimethyl-cyclohexyl isocyanate (IPDI), 1,4-cyclohexane diisocyanate and 4,4'-cyclohexylmethane diisocyanate; aliphatic diisocyanates such as methylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, and 1,2-ethylene diisocyanate; aliphatic triisocyanates such as 1,3,6-hexamethylenetriisocyanate; aromatic triisocyanates, such as 4,4',4"-triphenylmethane triisocyanate; polyisocyanates such as polymethylene-polyphenyl-isocyanate (PAPI); isocyanurates, such as the trimer of hexamethylenediisocyanate and the trimer of IPDI and mixtures thereof.

In the preparation of the fluorochemical polyurethane compounds of the invention it is preferred that not only difunctional isocyanates, i.e., isocyanates $A(NCO)_2$, are used, but that at least some higher functional, e.g., trifunctional isocyanate is employed.

This means that the fluorochemical polyurethane compounds of the invention are preferably not just linear compounds obtained from diisocyanates but contain at least some sites of branching due to the inclusion of tri- or tetraisocyanates. More preferably, at least about 50%, most preferably more than 90% of the isocyanates employed are triisocyanates.

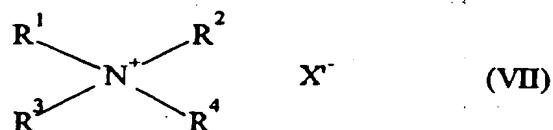
Difunctional chain extenders HX-B-XH suitable in the formation of the fluorochemical polyurethane compounds of the invention include difunctional alcohols, thiols and amines. A single compound or a mixture of different chain extenders may be used. Examples include diols such as 1,4-butanediol, 1,6-

hexanediol, 1-10-decanediol, 4,4'-isopropylidene diphenol (Bisphenol A); polyester diols, such as polycaprolactone diol, fatty acid dimer diols and poly(oxy)alkylenediols with an oxyalkylene group having 2 to 4 carbon atoms, such as $-OCH_2CH_2-$, $-O(CH_2)_4-$, $-OCH_2CH_2CH_2-$, $-OCH(CH_3)CH_2-$ and $-OCH(CH_3)CH(CH_3)-$ (preferably the oxyalkylene units in said poly(oxyalkylene) being the same, as in polypropyleneglycol or present as a mixture). In a preferred embodiment the group B comprises siloxane groups, such as dimethylsiloxane groups, which impart soft hand to the substrate treated with the fluorochemical polyurethane. Furthermore, the group B may be partially fluorinated in order to enhance the oil- and water-repellent characteristics of the compound.

Conventional isocyanate masking or blocking agents include alcohols such as methanol, ethanol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, t-butyl alcohol, n-amyl alcohol, t-amyl alcohol, 2-ethylhexanol, glycidol, (iso)stearylalcohol; aryl alcohols (e.g., phenols, cresols, nitrophenols, o- and p-chlorophenol, naphthols, 4-hydroxybiphenyl); C_2 to C_8 alkanone oximes (e.g., acetone oxime, butanone oxime); benzophenone oxime; aryl-thiols (e.g., thiophenol); organic carbanion active hydrogen compounds (e.g., diethyl malonate, acetylacetone, ethyl acetoacetate, ethylcyanoacetate); epsilon-caprolactone; primary or secondary amines (e.g., butyl amine); hydroxylamine; primary amino mercaptans and secondary amino mercaptans. A single compound or a mixture of different masking or blocking agents may be used. Particularly preferred blocking or masking agents include C_2 to C_8 alkanone oximes, e.g., 2-butanone oxime, monofunctional alcohols such as 2-ethylhexanol and (iso)stearylalcohol.

Step 2 is carried out under conventional urethane forming conditions. The reaction is carried out under dry conditions preferably in a polar solvent such as ethyl acetate, acetone, methyl ethyl ketone and methyl isobutyl ketone. Preferably the reaction is run in the presence of a catalyst. Preferred catalysts include tin salts such as dibutyltin dilaurate and stannous octoate. Suitable reaction temperatures will be readily determined by those skilled in the art based on the particular reagents, solvent, and catalysts being used.

The fluorochemical polyurethane compound of this invention can be applied using conventional application methods and can be used as an aqueous dispersion or alternatively it can be used as a treatment composition in a solvent. A dispersion will generally contain water, an amount of compound effective to provide repellent properties to a substrate treated therewith, and a surfactant in an amount effective to stabilize the dispersion. Water is preferably present in an amount of about 70 to about 20000 parts by weight based on 100 parts by weight of the compound of the invention. The surfactant is preferably present in an amount of about 1 to about 25 parts by weight, preferably about 5 to about 10 parts by weight, based on 100 parts by weight of the composition of the invention. Conventional cationic, nonionic, anionic, and zwitterionic surfactants are suitable. Preferred surfactants are ammonium surfactants (used alone or as mixtures with nonionic surfactants) having two long chain alkyl groups which can be represented by the general formula (VII):



wherein:

- R¹ and R² each and independently are long chain alkyl groups containing at least eight carbon atoms, preferably from 8 to 24 carbon atoms or benzyl groups.
- R³ and R⁴ each and independently are short chain alkyl groups having from 1 to 8 carbon atoms or hydrogen.
- X⁻ is an anion, preferably halogen (Cl⁻, Br⁻, I⁻), HSO₄⁻, CH₃COO⁻.

Surprisingly, it has been found that the use of said ammonium surfactants enhances the durability of the oil and water repellent properties and the LAD effect of the fluorochemical polyurethane compounds of the invention.

The amount of the treating composition applied to a substrate in accordance with this invention is chosen so that sufficiently high or desirable water and oil repellencies are imparted to the substrate surface, said amount usually being such that 0.01% to 5% by weight, preferably 0.05% to 2% by weight, based on the weight of the substrate, of fluorochemical treating agent is present on the treated substrate. The amount which is sufficient to impart desired repellency can be

determined empirically and can be increased as necessary or desired. In order to treat a substrate, the substrate can be immersed in the dispersion and agitated until it is saturated. The saturated substrate can then be run through a padder/roller to remove excess dispersion, dried in an oven at a relatively low temperature (e.g., 70°C) for a time sufficient to remove the dispersion medium (e.g., water, ethylene glycol, or a mixture thereof), and cured at a temperature and for a time sufficient to provide a cured treated substrate. This curing process can be carried out at temperatures between about 70°C and about 190°C depending on the particular system or application method used. In general, a temperature of about 170°C for a period of about 20 seconds to 3 minutes, preferably 1 to 2 minutes, is suitable. The cured treated substrate can be used as desired, e.g., incorporated or fashioned into a garment.

In order to improve fixing of the composition of the invention to a substrate, it is sometimes advantageous to include in the dispersion certain additives, polymers, thermo-condensable products and catalysts capable of promoting interaction with the substrate. Among these are the condensates or precondensates of urea or melamine with formaldehyde and glyoxal resins. Particular suitable additives and amounts thereof can be selected by those skilled in the art.

The substrates treated by the water and oil repellency imparting composition of this invention are not especially limited and include, e.g., textile fibers, fabrics, non-wovens, leather, paper, carpet, plastic, wood, metal, glass, concrete and stone. Preferred are fibers, woven or non-woven fabrics, carpets, leather and paper.

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

Examples

Formulation and Treatment Procedure

Treatment baths were formulated containing a defined amount of the fluorochemical treatment agent. Treatments were applied to the test substrates by padding to provide a concentration of 0.3% solids (based on fabric weight and indicated as SOF (solids on fabric)) and drying and curing at 170°C for 1.5 minutes unless otherwise indicated. Substrates used for the evaluation of treatments of this invention are all commercially available and are listed below:

PES/CO: Grey polyester/cotton 65/35, style No. 2681, obtained from Utexbel N.V., Ronse, Belgium

100% CO: bleached, mercerized cotton poplin, style No. 2286, obtained from Utexbel N.V., Ronse, Belgium

100% PAM: Polyamide microfiber, style No. 7819, obtained from Sofinal, Belgium

100% PES: Polyester microfiber, style No. 6145, obtained from Sofinal, Belgium

Acrylic Awning: Available from Dixon Constant, Wasquehal, France.

Respective data of water and oil repellency shown in the following Examples and Comparative Examples are based on the following methods of measurement and evaluation criteria:

Bundesmann Test

The impregnating effect of rain on treated substrates is determined using the Bundesmann Test Method (DIN 53888).

In this test, the treated substrates are subjected to a simulated rainfall, while the back of the substrate is being rubbed. The appearance of the upper exposed surface is checked visually after 1, 5 and 10 minutes and is given a rating between 1 (complete surface wetting) and 5 (no water remains on the surface). Besides the observation of the wetting pattern also the water absorption (% ABS) can be quantitatively measured. Well treated samples give low absorption results.

Spray Rating (SR)

The spray rating of a treated substrate is a value indicative of the dynamic repellency of the treated substrate to water that impinges on the treated substrate. The repellency is measured by Standard Test Number 22, published in the 1985 Technical Manual and Yearbook of the American Association of Textile Chemists and Colorists (AATCC), and is expressed in terms of 'spray rating' of the tested substrate. The spray rating is obtained by spraying 250 ml water on the substrate from a height of 15 cm. The wetting pattern is visually rated: using a 0 to 100 scale, where 0 means complete wetting and 100 means no wetting at all.

Oil Repellency (OR)

The oil repellency of a treated substrate is measured by the American Association of Textile Chemists and Colorists (AATCC) Standard Test Method No. 118-1983, which test is based on the resistance of a treated substrate to penetration by oils of varying surface tensions. Treated substrates resistant only to Nujol® mineral oil (the least penetrating of the test oils) are given a rating of 1, whereas treated substrates resistant to heptane (the most penetrating of the test oils) are given a rating of 8. Other intermediate values are determined by use of other pure oils or mixtures of oils, as shown in the following table.

Standard Test Liquids

AATCC Oil Repellency Rating Number	Compositions
1	Nujol® mineral oil
2	Nujol®/n-hexadecane 65/35
3	n-Hexadecane
4	n-Tetradecane
5	n-Dodecane
6	n-Decane
7	n-Octane
8	n-Heptane

Laundering Procedure

The procedure set forth below was used to prepare treated substrate samples designated in the examples below as "5 Home Launderings (5HL)".

A 230 g sample of generally square, 400 cm² to about 900 cm² sheets of treated substrate was placed in a washing machine along with a ballast sample (1.9 kg of 8 oz fabric in the form of generally square, hemmed 8100 cm² sheets). A commercial detergent ("Sapton", available from Henkel, German, 46 g) is added and the washer is filled to high water level with hot water (40°C +/- 3°C). The substrate and ballast load is washed five times using a 12-minute normal wash cycle followed by five rinse cycles and centrifuging. The samples are not dried between repeat cycles.

Air-dry Procedure: The substrate is hung on a support means and dried at room temperature (about 20°C) during 24 hours.

Ironing cycle: After drying, the samples are pressed using an iron with the temperature set for the fiber of the substrate.

The laundering procedure was followed by performance tests such as the Water Spray Test (SR and % absorption) and the Oil Repellency Test (OR).

Dry Clean Procedure

The ability of a substrate treated with a compound of this invention to continue performing its function after being subjected to dry cleaning was determined using a modification of "3M Laboratory Dry Cleaning Procedure I", Scotchgard® Protector, 3M Test Methods, October 1, 1988. Five dry cleanings were carried out without detergent (indicated as 5DC). This was followed by performance tests such as the Water Spray Test (SR) or the OIL Repellency Test (OR) described above.

Spot Cleaning Air-dry Test

Treated fabrics were tested for their ability to withstand home spot cleaning. For this test, the fabric was first rubbed with soap (55% "Dreft" detergent, available from Procter and Gamble) after which the fabric was given one rinse cycle in a home laundering machine. After the fabric was dried at room temperature for 24

hours, performance tests such as the Oil Repellency Test (OR) and Water Spray test (SR) described above were done.

Evaluation of Fabric "Hand" or Softness

Treated fabrics were rated for their "hand", i.e., their softness, smoothness, pliability and fluffiness to the touch, as this feature is important for the comfort and aesthetic appeal of repellent textile substrates. A scale of 10 to 1 was used, where a rating of 10 was given to those treatments which left the fabric the softest, while a rating of 1 was given to those treatments which gave the fabric the harshest hand (i.e., provided a rough, stiff, cardboard-like feel). The ratings in between were assigned to intermediate hand values. The ratings were an average of the evaluation by a test panel (8-10 persons).

Abbreviations

The following abbreviations and trade names are used in the examples:

MEKO: methyl ethyl ketoxime or 2-butanone oxime

Arcol P1004: polypropylene glycol (Mw 430), available from Arco Chemical Industries

Bisphenol A: 4,4'-isopropylidene diphenol

BuFOSEMA: N-butyl perfluorooctyl sulfonamidoethyl (meth)acrylate

MeFOSEMA: N-methyl perfluorooctyl sulfonamidoethyl (meth)acrylate

EtFOSBA: N-methyl perfluorooctyl sulfonamidobutyl acrylate

EtFOSE: N-ethyl perfluorooctyl sulfonamidoethanol

EHMA: ethylhexyl methacrylate

N-MAM: $\text{HOCH}_2\text{NHC(O)CH=CH}_2$ (48 wt% aqueous solution)

Voranate M220 or PAPI: polymethylene polyphenyl isocyanate, available from Dow Chemical, Terneuzen, The Netherlands

Ethoquad HT-25: methyl polyoxyethylene (15) hydrogenated tallow ammonium chloride, available from Akzo, Littleborough, UK

Arquad T-50: tallow trimethyl ammoniumchloride, available from Akzo, Littleborough, UK

Arquad 2HT-75: dimethyl-dihydrogenated tallow ammonium chloride; available from Akzo, Littleborough, UK

Atpol E5721: alkylethoxylate, available from ICI, Wilton, UK

Rewopon IM OA: imidazoline type surfactant, available from Rewo, Germany

Ethomeen HT25: polyoxyethylene (15) hydrogenated tallow amine, available from Akzo, Littleborough, UK

Varine C: imidazoline type surfactant, available from Sherex Chemical Co., Dublin, Ohio, USA

Fluowet AC812: telomer-type fluorochemical acrylate

$C_nF_{2n+1}-CH_2CH_2OC(O)CH=CH_2$, available from Hoechst AG, Germany

Telomer acrylate: $C_nF_{2n+1}-CH_2CH_2OC(O)CH=CH_2$ wherein n is 9.4

RSH: 2-mercaptoethanol

FOA: perfluorooctyl dihydroacrylate

FOMA: perfluorooctyl dihydromethacrylate

Si-acrylate: Shin-Etsu X-248201, available from Shin-Etsu Chemical Co., Tokyo, Japan

Wacker IM11 and VP1610: alpha,omega-hydroxy organofunctional

polydimethylsiloxanes, available from Wacker Chemie, Munchen, Germany

ECF: electrochemical fluorination

Terathane 650: polytetramethylene oxide, available from Dupont, USA

i-BMA: isobutylmethacrylate

ODA: octadecylacrylate

VCl₂: vinylidene chloride

All parts, ratios, percentages, etc., in the following examples and the rest of the specification, are by weight unless otherwise noted.

A. Synthesis of Intermediate Fluorochemical Oligomers

The fluorochemical oligomers listed in Table I were prepared according to the general procedure as described for the synthesis of MeFOSEA/2-mercaptoethanol 4/1.

A 3 l reaction flask, equipped with 2 reflux condensers, a mechanical Teflon polymer-coated blade stirrer, a thermometer, a nitrogen inlet and vacuo outlet, was charged with 2.4 moles MeFOSEA and 987 g ethylacetate. The mixture was heated to 40°C until all fluorochemical monomer was dissolved. 0.6 moles 2-mercaptoethanol and 0.15% AIBN were added and the solution was heated to 80°C, while stirring at 160 rpm. The reaction was run under nitrogen atmosphere at 80°C during 16 hours, after which more than 95% conversion was obtained.

Following the above described method, the different fluorochemical oligomers listed in Table 1 were synthesized.

Table 1: Composition of Fluorochemical Oligomers

FC-Oligomer	Monomer Composition	Molar Ratio
FC-1	MeFOSEA/RSH	8/1
FC-2	MeFOSEA/RSH	4/1
FC-3	FluowetAC812/RSH	4/1
FC-4	Telomer acrylate/RSH	4/1
FC-5	MeFOSEA/Telomer acrylate/RSH	2/2/1
FC-6	MeFOSEA/ODA/RSH	2/2/1
FC-7	MeFOSEMA/RSH	4/1
FC-8	MeFOSEA/RSH	2/1
FC-9	MeFOSEA/iBMA/RSH	6/2/1
FC-10	BuFOSEA/RSH	4/1
FC-11	EtFOSEA/RSH	4/1
FC-12	EtFOSEMA/RSH	4/1
FC-13	Fluowet AC812/iBMA/RSH	3/1/1
FC-14	MeFOSEA/iBMA/RSH	3/1/1
FC-15	FOA/RSH	4/1
FC-16	MeFOSEA/ODA/VC1 ₂ /RSH	5/2/1/1
FC-17	Fluowet AC812/ODA/VC1 ₂ /RSH	5/2/1/1
FC-18	FOMA/RSH	4/1

FC-Oligomer	Monomer Composition	Molar Ratio
FC-19	MeFOSBA/RSH	4/1
FC-20	MeFOSEA/EHMA/RSH	3/1/1
FC-21	MeFOSEA/Si-acrylate/RSH	3.75/0.25/1
FC-22	MeFOSEA/HSCH ₂ (HS)CHCH ₂ OH	8/1
FC-23	Fluowet AC812/RSH	6/1
FC-24	Fluowet AC 812/iBMA/RSH	6/2/1
FC-25	Fluowet AC812/MeFOSEA/RSH	3.2/0.8/1
FC-26	Fluowet AC812/MeFOSEA/RSH	2.4/1.6/1

Examples 1-39

Synthesis of Fluorochemical Polyurethanes

The fluorochemical oligomers, prepared in step A, were further reacted with isocyanate derivatives, chain extenders and blocking agents according to the general method outlined below for the synthesis of PAPI/FC-2/Arcol P1004/MEKO 3/2/2/3 (FCU-1):

A 500 ml 3-necked flask was equipped with a Dean-Stark condenser, a mechanical Teflon polymer coated blade stirrer, a thermometer and a nitrogen inlet. Fluorochemical oligomer FC-2 (0.04 mole or 164.4 g of the 60% solution in ethylacetate, prepared in step A), Arcol polyol P1004 (0.04 mole) and 152 g ethylacetate were charged to the flask. 60 g Ethylacetate was azeotropically distilled off via the Dean-Stark condenser, so as to obtain a 40% solution (total solids). After cooling to 55°C, the Dean-Stark condenser was replaced by a normal reflux condenser. 0.06 moles PAPI was added as well as dibutyltindilaurate catalyst (0.025% on solids). The solution was gently heated to 75°C. After the reaction exotherm, the mixture was heated at 75°C during 8 hours. The reaction mixture was cooled to 55°C and methylethylketoxime (0.06 mole) was added gradually over 5 minutes. The reaction was completed under stirring for another hour at 75°C. The FTIR spectrum showed that all isocyanate absorptions had disappeared. The final product, a clear brownish solution at 75°C, became partly solid when cooled below 55°C.

Following the above described method, the different fluorochemical polyurethanes listed in Table 2 were prepared. In some cases more than one fluorochemical oligomer, more than one chain extender or more than one blocking or masking agent was used.

Table 2. Composition of Fluorochemical Polyurethanes (FCU)

FCU-No.	Composition	Molar Ratio
FCU-1	PAPI/FC-2/Arcol P1004/MEKO	3/2/2/3
FCU-2	PAPI/FC-2/1,2-propanediol/MEKO	3/2/2/3
FCU-3	PAPI/FC-2/2-glycerolmonostearate/MEKO	3/2/2/3
FCU-4	PAPI/FC-2/2-ethyl(1,3)hexanediol/MEKO	3/2/2/3
FCU-5	PAPI/FC-14/FC-13/Arcol P1004/MEKO	3/1/1/2/3
FCU-6	PAPI/FC-1/Arcol P1004/MEKO/C ₁₈ H ₃₇ OH	4/2/3/3/1
FCU-7	PAPI/FC-20/Arcol P1004/MEKO	3/2/2/3
FCU-8	PAPI/FC-21/Arcol P1004/MEKO	3/2/2/3
FCU-9	PAPI/FC-2/Arcol P1004/MEKO/C ₁₈ H ₃₇ OH	5/3/4/3/1
FCU-10	PAPI/FC-1/Arcol P1004/MEKO/C ₁₈ H ₃₇ OH	5/2/4/3/2
FCU-11	PAPI/FC-1/Arcol P1004/MEKO/C ₈ H ₁₇ OH	5/2/4/3/2
FCU-12	PAPI/FC-1/Arcol P1004/MEKO	5/2/4/5
FCU-13	PAPI/FC-15/Arcol P1004/MEKO/C ₁₈ H ₃₇ OH	3/2/2/2/1
FCU-14	PAPI/FC-18/Arcol P1004/MEKO	3/2/2/3
FCU-15	PAPI/FC-17/Arcol P1004/MEKO/C ₁₈ H ₃₇ OH	3/1/2/3/1
FCU-16	PAPI/FC-2/Terathane 650/MEKO	3/2/2/3
FCU-17	PAPI/FC-3/Terathane 650/MEKO	3/2/2/3
FCU-18	PAPI/FC-3/Arcol P1004/MEKO	3/2/2/3
FCU-19	PAPI/FC-3/WackerIM11/MEKO	3/2/2/3
FCU-20	PAPI/FC-17/Wacker IM11/MEKO/C ₁₈ H ₃₇ OH	3/1/2/3/1
FCU-21	PAPI/FC-16/Wacker IM11/MEKO/C ₁₈ H ₃₇ OH	3/1/2/3/1
FCU-22	PAPI/FC-2/Bisphenol A/MEKO/C ₁₈ H ₃₇ OH	3/2/2/2/1
FCU-23	PAPI/FC-3/Bisphenol A/MEKO/C ₁₈ H ₃₇ OH	3/2/2/2/1
FCU-24	PAPI/FC-4/Arcol P1004/MEKO	3/2/2/3
FCU-25	PAPI/FC-1/Arcol P1004/C ₁₈ H ₃₇ OH/MEKO	4/2/3/1/3

FCU-No.	Composition	Molar Ratio
FCU-26	PAPI/FC-1/Arcol P1004/Wacker IM11/C ₁₈ H ₃₇ OH/MEKO	4/2/1.5/1.5/1/3
FCU-27	PAPI/FC-4/Bisphenol A/MEKO	3/2/2/3
FCU-28	PAPI/FC-4/Arcol P1004/MEKO	3/2/2/3
FCU-29	PAPI/FC-7/Arcol P1004/MEKO	3/2/2/3
FCU-30	PAPI/FC-10/Arcol P1004/MEKO	3/2/2/3
FCU-31	PAPI/FC-11/Arcol P1004/MEKO	3/2/2/3
FCU-32	PAPI/FC-12/Arcol P1004/MEKO	3/2/2/3
FCU-33	PAPI/FC-9/Arcol P1004/MEKO/C ₁₈ H ₃₇ OH	3/1/2/3/1
FCU-34	PAPI/FC-14/Arcol P1004/MEKO	3/2/2/3
FCU-35	PAPI/FC-2/Arcol P1004/C ₈ H ₁₇ OH	3/2/2/3
FCU-36	PAPI/FC-2/VP1610/MEKO	3/2/2/3
FCU-37	PAPI/FC-2/Bisphenol A/MEKO	3/2/2/3
FCU-38	PAPI/FC-4/FC-2/Bisphenol A/MEKO	3/1/1/2/3
FCU-39	PAPI/FC-5/Bisphenol A/MEKO	3/2/2/3

Emulsification of the Fluorochemical Polyurethanes

The fluorochemical polyurethanes were emulsified using different surfactants or mixtures of surfactants, following the general procedure as described for a mixture of Arquad 2HT-75 and Atpol E5721 surfactants.

Arquad 2HT-75 (3.5% based on fluorochemical polyurethane solids) was dissolved in a solution of the fluorochemical polyurethane. This solution was heated to 65°C and subsequently added to an aqueous mixture of Atpol E5721 (3.5% of fluorochemical solids) in deionized water. This mixture was stirred vigorously for 5 minutes. The formed pre-emulsion was then emulsified by immersion of an ultrasound probe (Branson 250 Sonifier) for 3 minutes at maximum output. The ethylacetate was distilled off with a rotary evaporator at 55°C, using waterjet vacuum. An aqueous emulsion of about 20% solids was obtained. The emulsion thus formed was used to treat fabrics.

Examples 40-67

In the following Examples, fluorochemical polyurethane compositions were prepared according to the previously described general procedure. Except for Examples 53 and 67, the polyurethanes were emulsified in water using 7% Arquad 2HT75 emulsifier. Polyester microfiber and polyester/cotton blend were treated with the fluorochemical dispersions so as to give 0.3% SOF. After treatment, the fabrics were cured at 170°C for 1.5 minutes. The fluorochemical polyurethane compositions evaluated and the results of oil and water repellency tests are given in Tables 3 and 4.

Table 3: Oil and Water Repellency of PES Treated with Fluorochemical
Polyurethane Compositions

Ex No.	FCU	Initial		Bundesmann				5HL air-dry			5HL Iron		5DC	
		OR	SR	1'	5'	10'	% abs	OR	SR	% abs	OR	SR	OR	SR
40	FCU-1	5	100	5	5	4	6	1	70	9	1	100	5	100
41	FCU-2	4	100	5	5	3	12	1	70	5	4	100	4	100
42	FCU-3	4	100	5	5	5	6	1	70	6	3	100	2	100
43	FCU-4	5	100	5	5	4	11	1	70	5	4	100	4	100
44	FCU-6	5	100	5	5	4	12	1	70	8	4	100	4	100
45	FCU-7	5	100	5	3	2	18	1	70	15	3	100	3	100
46	FCU-8	2	100	5	2	1	21	0	0	9	2	100	2	100
47	FCU-10	4	100	5	5	5	8	1	70	12	3	100	4	100
48	FCU-11	5	100	5	5	5	6	1	80	9	4	100	4	100
49	FCU-12	5	100	5	5	4	8	1	70	8	4	100	4	100
50	FCU-14	4	90	1	1	1	21	2	70	6	3	90	2	90
51	FCU-15	4	100	5	4	3	8	1	100	0	3	100	2	100
52	FCU-17	6	100	3	2	2	15	3	80	1	5	100	6	100
53	FCU-18	5	100	5	5	5	7	2	100	0	5	100	5	100

Note: Example 53 was made by using a mixture of 3.5% Arquad 2HT 75 and 3.5% Atpol E5721 as surfactants.

Table 4: Oil and Water Repellency of PES/CO Treated with Fluorochemical

Polyurethane Compositions

Ex No.	FCU	Initial		Bundesmann				5HL air-dry			5HL Iron		5DC	
		OR	SR	1'	5'	10'	% abs	OR	SR	% abs	OR	SR	OR	SR
54	FCU-1	6	100	5	5	4	10	2	80	7	6	100	6	100
55	FCU-2	6	100	5	3	2	17	3	90	2	6	100	6	100
56	FCU-3	6	100	5	4	1	18	2	80	7	6	100	6	100
57	FCU-4	6	100	5	4	3	18	3	90	3	6	100	6	100
58	FCU-6	6	100	5	3	2	16	2	70	8	6	100	6	100
59	FCU-7	6	100	5	3	2	18	2	70	9	6	100	5	100
60	FCU-8	5	100	5	3	1	19	1	80	4	5	100	5	100
61	FCU-10	6	100	5	4	3	14	2	80	8	6	100	6	100
62	FCU-11	6	100	5	4	2	19	2	80	8	6	100	6	100
63	FCU-12	6	100	5	4	3	13	2	80	5	6	100	6	100
64	FCU-14	5	100	1	1	1	21	3	80	7	5	100	5	90
65	FCU-15	6	100	5	4	4	9	2	100	2	6	100	5	100
66	FCU-17	6	100	3	1	1	14	6	90	4	6	100	6	100
67	FCU-18	7	100	5	4	3	16	6	100	3	7	100	7	100

Note: Example 67 was made by using a mixture of 3.5% Arquad 2HT 75 and 3.5% Atpol E5721 as surfactants.

The data show that surprisingly, fluorochemical polyurethane compositions according to the invention show a real laundry air-dry effect. High water repellency (at least a SR of 70, many times even 90 or 100 and low % water absorption) were observed even after 5 launderings without the need for ironing the dried samples.

5

Examples 68-78

In examples 68 to 78 the same kind of experiment described in Examples 40-67 was repeated with the fluorochemical polyurethanes tested in Tables 5 and 6. This time, the compositions, emulsified with 7% Arquad 2HT75 were tested on polyamide microfiber (0.3% SOF) and on cotton (0.6% SOF). The results of repellency after treatment are given in Tables 5 and 6.

10

Table 5: Oil and Water Repellency of PA Treated with Fluorochemical
Polyurethane Compositions

Ex	FCU	Initial		Bundesmann				5HL air-dry			5HL Iron--		5DC	
No.		OR	SR	1'	5'	10'	% abs	OR	SR	% abs	OR	SR	OR	SR
68	FCU-27	7	100	5	5	4	9	2	80	8	6	100	6	100
69	FCU-28	6	100	5	5	3	15	2	70	8	5	100	6	100
70	FCU-29	6	100	5	3	3	20	1	70	14	3	100	3	100
71	FCU-32	5	100	3	1	1	34	1	60	16	2	100	2	100
72	FCU-33	6	100	5	5	3	23	1	70	20	5	100	5	100
73	FCU-34	6	100	5	1	1	34	2	60	18	5	100	5	100

Table 6: Oil and Water Repellency of CO Treated with Fluorochemical

Polyurethane Compositions

Ex No.	FCU	Initial		Bundesmann				5HL air-dry			5HL Iron		5DC	
		OR	SR	1'	5'	10'	% abs	OR	SR	% abs	OR	SR	OR	SR
74	FCU-27	6	100	5	3	2	24	4	100	4	6	100	6	100
75	FCU-28	6	100	5	4	3	23	4	90	5	6	100	6	100
76	FCU-29	5	100	3	2	1	29	2	80	8	4	100	4	90
77	FCU-33	6	100	2	1	1	29	0	70	17	5	90	5	90
78	FCU-34	5	90	2	1	1	30	0	70	15	5	90	5	80

Again, good durable repellency properties were obtained, indicating that the fluorochemical polyurethanes had good repellency both on synthetic and on natural fibers.

5 Examples 79-84

10 [Examples 79 to 84 illustrate the influence of the blocking or masking agent or repellency properties. In Examples 79, 81, and 83, an oxime blocking agent was used and in Examples 80, 82, and 84 a monofunctional alcohol was used. The fluorochemical polyurethanes were emulsified using 7% Arquad 2HT75. The results of repellency properties of various substrates treated with the composition are given in Table 7.

Table 7. Repellency Properties of Fabrics Treated with
Fluorochemical Polyurethanes

Ex	FCU	Initial		Bundesmann			5HL Iron		5DC	
No.	No.	OR	SR	1'	5'	10'	%	OR	SR	SR
<u>Polyester microfibre</u>										
79	FCU-1	5	100	5	5	5	6	4	100	5 100
80	FCU-35	5	100	5	5	4	10	5	100	5 90
<u>Polyamide microfibre</u>										
81	FCU-1	6	100	4	2	1	33	5	100	6 100
82	FCU-35	6	100	5	1	1	37	6	90	6 90
<u>PES/CO</u>										
83	FCU-1	6	100	4	3	2	19	6	100	6 100
84	FCU-35	6	100	2	1	1	20	6	80	6 80

The results indicate that compositions prepared from either an oxime or with a monofunctional alcohol as the blocking/masking agent provides good and durable water and oil repellency properties.

5 Examples 85-90

Examples 85 to 90 illustrate the influence of a siloxane chain extender.

Siloxanes are known to impart softness to the treated fabric. However, in many cases, siloxanes have a negative impact on the repellency properties of the treatment. In Examples 85 to 90, fluorochemical polyurethanes were applied to

10 PES, PA and to PES/CO. The hand or softness of the treated fabrics was evaluated by a panel of 8 persons. The average value is recorded in Table 8.

Table 8: Repellency Properties and Softness of Treated Fabrics

Ex	FCU- No.	Initial		Bundesmann				5HL Iron		5DC		Softne ss
No.		OR	SR	1'	5'	10'	% abs	OR	SR	OR	SR	
<u>Polyester microfibre</u>												
85	FCU-1	5	100	5	5	5	3	4	100	2	100	4
86	FCU-36	3	100	5	5	4	5	2	100	3	100	7
<u>Polyamide microfibre</u>												
87	FCU-1	5	100	5	3	1	30	5	100	5	100	3
88	FCU-36	4	100	5	3	2	31	4	100	4	100	8
<u>PES/CO</u>												
89	FCU-1	6	100	4	4	3	14	6	100	6	100	4
90	FCU-36	6	100	4	2	1	17	5	100	5	90	8

Note: The softness of the untreated fabrics was rated as follows: PES: 6; PA: 6 and PES/CO: 4.

The results indicate that, although a remarkable increase in softness was obtained by incorporating a siloxane chain extender, surprisingly, the repellent properties were not much influenced.

5 Examples 91-94

The same kind of experiment as that described in Examples 85 to 90 was repeated with fluorochemical polyurethanes that were prepared starting from other fluorochemical oligomers. The results are given in Table 9.

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Table 9: Repellency Properties and Softness of Treated Fabrics

Ex	FCU-No.	Initial		Bundesmann				5HL air-dry			5DC		Softne ss
No.		OR	SR	1'	5'	10'	% abs	OR	SR	%abs	OR	SR	
<u>PES/CO</u>													
91	FCU-19	7	100	5	5	4	9	5	100	1	6	100	9
92	FCU-20	6	100	5	5	5	8	2	100	1	5	100	
<u>Polyamide microfiber</u>													
93	FCU-19	5	100	5	5	4	12	2	70	5	--	--	7
94	FCU-20	4	100	5	5	3	13	1	70	6	--	--	

Note: softness of untreated fabrics: PES/CO: 6; PA: 7.

The data shows that the addition of siloxane extender did not harm the oil and water repellency properties of the treatment compositions. The treated fabrics prepared for these examples not only had a very soft feeling, but also showed high repellency properties and a surprisingly high laundry air-dry performance.

5

Examples 95 to 98

In Examples 95 to 98, the influence of the fluorochemical monomer (used to make the fluorochemical polyurethane), on the performance of the treating agent was evaluated. Therefore, Example-95 was made starting from sulfonamido group containing fluorochemical monomer; Example 96 was made starting from telomer derived fluorochemical; in Example 97 a fluorochemical polyurethane was made starting from a mixture of fluorochemical oligomers and in Example 98 the fluorochemical oligomer was made starting from a mixture of sulfonamido type and telomer derived fluorochemical monomers. The treating compositions, emulsified with 7% Arquad 2HT75 were evaluated on PES. The results of repellency properties of the treated fabrics are given in Table 10.

10

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Table 10

Ex No.	FCU-No.	Initial		Bundesmann				5HL air-dry			5 HL Iron		5 DC	
		OR	SR	1'	5'	10'	% abs	OR	SR	%	OR	SR	OR	SR
95	FCU-37	5	100	5	5	4	8	1	70	abs	4	100	4	100
96	FCU-27	6	100	5	5	5	5	3	100	0	5	100	5	100
97	FCU-38	5	100	5	5	4	6	2	80	1	4	100	4	100
98	FCU-39	5	100	5	4	3	10	2	80	2	4	100	4	100

The results indicate that the best performance, especially LAD, was obtained with telomer derived fluorochemical urethanes.

Examples 99 to 114

- 5 Examples 99 to 114 illustrate the influence of the surfactant system used to make a fluorochemical polyurethane dispersion on repellency properties. For this study, fluorochemical polyurethane FCU-1 (PAPI/FC-2/Arcol P1004/MEKO 3/2/2/3) was emulsified with different systems. The compositions were tested on PES/CO and on PES. A list of surfactants tested is given below. The results of
10 repellency of the treated fabrics are given in Table 11.

Surfactants:

- S1. 7% Arquad 2HT75
S2. 3.5% Arquad 2HT75 + 3.5% Atpol E5721
15 S3. 3.5% Arquad 2HT75 + 3.5% Silwet C90
S4. 7% Ethoquad HT25
S5. 7% Arquad T50
S6. 7% Rewopon IM-OA
S7. 7% Ethomeen HT25
20 S8. 7% Varine C.

Table 11: Influence of Surfactant System

Ex	Surfactant t	Initial		Bundesmann				5HL Iron		5DC	
		OR	SR	1'	5'	10'	% abs	OR	SR	OR	SR
99	S1	5	100	5	5	5	9	4	100	4	100
100	S2	5	100	5	5	5	7	4	100	3	100
101	S3	5	100	5	5	5	6	4	100	3	100
102	S4	5	80	1	1	1	26	4	80	4	80
103	S5	5	80	1	1	1	29	4	70	3	80
104	S6	5	80	1	1	1	26	4	70	5	80
105	S7	6	80	1	1	1	25	5	70	5	70
106	S8	5	90	1	1	1	19	4	80	5	80
<u>PES/CO</u>											
107	S1	6	100	4	3	2	19	6	100	6	100
108	S2	6	100	3	1	1	20	6	100	6	80
109	S3	6	100	3	2	1	19	6	90	6	90
110	S4	6	90	1	1	1	23	6	80	6	80

Ex	Surfactant t	Initial		Bundesmann				SHL Iron		SDC	
No.		OR	SR	1'	5'	10'	% abs	OR	SR	OR	SR
99	S1	5	100	5	5	5	9	4	100	4	100
100	S2	5	100	5	5	5	7	4	100	3	100
101	S3	5	100	5	5	5	6	4	100	3	100
102	S4	5	80	1	1	1	26	4	80	4	80
103	S5	5	80	1	1	1	29	4	70	3	80
104	S6	5	80	1	1	1	26	4	70	5	80
105	S7	6	80	1	1	1	25	5	70	5	70
106	S8	5	90	1	1	1	19	4	80	5	80
<u>PES/CO</u>											
111	S5	6	80	1	1	1	29	6	70	6	70
112	S6	6	80	1	1	1	27	6	70	6	70
113	S7	6	80	1	1	1	23	6	80	6	80
114	S8	6	90	2	1	1	20	6	80	6	70

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Surprisingly, the data shows that fluorochemical polyurethanes emulsified with ammonium surfactants having two long chain alkyl groups, such as Arquad 2HT75, had superior properties to fabrics treated with compositions prepared from the same fluorochemical polyurethanes and conventional emulsifiers known in the art. Not only initial repellency is better, but also the durability increased and laundry air-dry performance was better.

Examples 115 to 126

Examples 115 to 126 illustrate the influence of the cure temperature on the performance of the fluorochemical polyurethane treatments on different substrates (0.3% SOF). The fluorochemical polyurethane tested was FCU-19 (PAPI/FC-3/Wacker IM 11/MEKO 3/2/2/3). After treatment, the substrates were cured for 1.5 minutes at different temperatures between 90°C and 150°C. The results are given in Table 12.

Table 12: Influence of Curing Temperature on Repellent Performance

Ex	FCU	Cure Temp	Initial		Bundesmann				5HL iron		5 DC	
No.			OR	SR	1'	5'	10'	% abs	OR	SR	OR	SR
<u>PES/CQ</u>												
115	FCU-19	90	5	70	1	1	1	/	5	80	5	80
116		110	6	80	1	1	1	32	5	80	5	80
117		130	6	100	4	3	2	16	5	90	5	90
118		150	6	100	4	3	2	12	5	90	6	90
<u>Polyamide microfibrer</u>												
119	FCU-19	90	2	80	1	1	1	/	2	80	2	80
120		110	4	90	2	1	1	36	2	80	3	90
121		130	4	100	5	4	3	20	2	90	4	90
122		150	4	100	4	4	3	28	3	90	4	90
<u>Polyester microfibrer</u>												
123	FCU-19	90	4	100	5	5	5	10	3	90	3	80
124		110	5	100	5	5	5	8	3	100	3	80
125		130	5	100	5	5	5	3	4	100	3	90
126		150	5	100	5	5	5	7	4	100	3	100

Note: / = has not been measured, were completely wet.

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Examples 127 to 130

Examples 127 to 130 illustrate the ability of fabrics treated with the composition of this invention to withstand a home spot cleaning test.

- Fluorochemical polyurethane FCU-1 (PAPI/FC-2/Arcol P1004/MEKO) and
 5 FCU-19 (PAPI/FC-3/Wacker IM11/MEKO) were used to treat cotton and upholstery acrylic awning. The fluorochemical polyurethanes were applied at 0.4% SOF. Curing was done at 150°C during 3 minutes. The performance tests were done before and after spot cleaning test. The results are given in Table 13.

10 Table 13: Resistance of Treated Fabrics Against Spot Cleaning Test

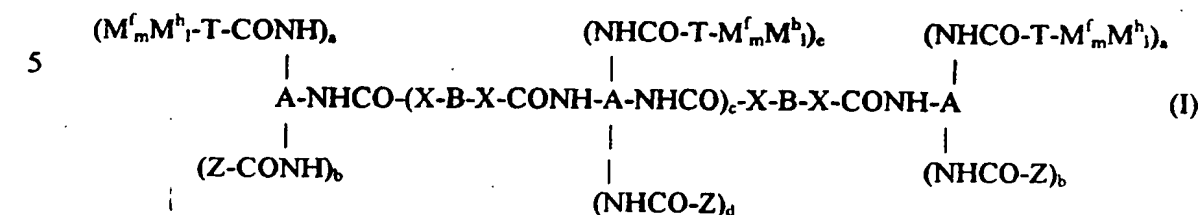
Ex No.	FCU-No.	Oil Repellency (OR)		Spray Rating (SR)	
		Initial	Spot Clean	Initial	Spot Clean
Acrylic awning					
127	FCU-1	5	100	4	80
128	FCU-19	6	100	5	90
Upholstery Cotton					
129	FCU-1	5	90	3	90
130	FCU-19	6	100	4	100

The results indicate that even after spot cleaning, high performance is still provided.

- Various modifications and alterations of this invention will become apparent
 15 to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

We claim:

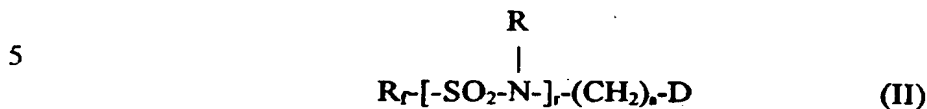
1. A fluorochemical polyurethane compound of formula (I)



wherein:

- M_m^fM_l^h is a fluorochemical oligomer, comprising m units derived from a fluorochemical monomer and l units derived from a fluorine-free monomer, wherein the fluorochemical monomers and the fluorine-free monomers may be the same or different;
- m has the value from 2 to 40;
- l has a value from 0 to 20;
- T is an organic linking group obtained by removing a hydrogen atom from a chain transfer agent, and the residues T may be the same or may be different;
- Z is the residue obtained by removing a hydrogen atom from an organic masking or blocking group, and the residues Z may be the same or may be different;
- A is a di-, tri- or tetravalent residue obtained by removing 2, 3 or 4 -NCO groups from a corresponding isocyanate, and the residues A may be the same or may be different;
- B is a divalent organic residue obtained by removing the 2 X-H groups from a difunctional active hydrogen compound HX-B-XH , wherein X is O, NH or S, and the residues B may be the same or may be different;
- a has a value from 1 to 3 and b has a value from 0 to 2, with the proviso that $a+b$ has a value from 1 to 3;
- c has a value from 0 to 30;
- d and e have a value from 0 to 2, provided that $d+e$ is not greater than 2.

2. A fluorochemical polyurethane compound according to claim 1, wherein the fluorochemical oligomer is derived from a fluorochemical monomer of the formula (II):



wherein R_f is $\text{C}_n\text{F}_{2n+1}$ with n being 3 to 18;

r is 0 or 1;

s is 1 to 8;

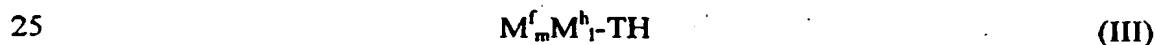
10 D is a group comprising a radically polymerizable unsaturated residue; and R is methyl or ethyl.

3. A fluorochemical polyurethane compound according to claims 1 or 2, wherein not all of the residues A are difunctional.

4. A fluorochemical polyurethane compound according to claim 3, wherein more than 90% of the residues A are trifunctional.

5. A fluorochemical polyurethane compound of any one of claims 1 to 4, wherein the residue B comprises siloxane groups.

6. A method of preparing a fluorochemical polyurethane compound of formula (I) which comprises reacting a fluorochemical oligomer of the formula (III)



wherein

- $\text{M}_m^f \text{M}_1^h$ is a fluorochemical oligomer, comprising m units derived from a fluorochemical monomer and 1 units derived from a fluorine-free monomer, wherein the fluorochemical monomers and the fluorine-free monomers may be the same or different;

- m has the value from 2 to 40;

- 1 has a value from 0 to 20;

- T is an organic linking group obtained by removing a hydrogen atom from a chain transfer agent, and the residues T may be the same or may be different;
with

(A) at least one isocyanate of formula (IV)

5
$$A(NCO)_x \quad (IV)$$

wherein A is a di- tri- or tetravalent residue obtained by removing 2, 3 or 4 -NCO groups from a corresponding isocyanate, and the residues A may be the same or may be different; and

x is 2 to 4;

10 (B) at least one bifunctional active hydrogen compound of formula (V)

$$HX-B-XH \quad (V)$$

wherein B is a divalent organic residue obtained by removing the 2 X-H groups from a difunctional active hydrogen compound HX-B-XH, wherein X is O, NH or S, and the residues B may be the same or may be different;

15 and

(C) at least one compound of formula (VI)

$$Z-H \quad (VI)$$

wherein Z is the residue obtained by removing a hydrogen atom from an organic masking or blocking group, and the residues Z may be the same or may be different.

20

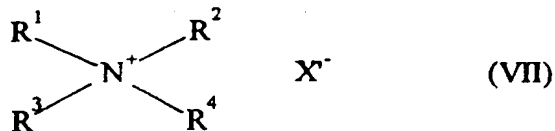
7. A composition comprising a fluorochemical polyurethane compound according to any one of claims 1 to 5 suitable to impart durable oil- and water-repellency and good laundry air-dry performance to substrates treated therewith.

25

8. A composition according to claim 7 additionally comprising a surfactant.

9. A composition according to claim 8 wherein the surfactant is an ammonium surfactant of formula (VII):

30



wherein:

-R¹ and R² each and independently are long chain alkyl groups containing at least eight carbon atoms;

5 -R³ and R⁴ each and independently are selected from the group consisting of short chain alkyl groups having from 1 to 8 carbon atoms or hydrogen; and

- X⁻ is an anion.

10 10. The use of a compound according to any one of claims 1 to 5 or of a composition according to any one of claims 7 to 9 to impart durable oil- and water-repellency and good laundry air-dry performance to substrates treated therewith.

11. The use according to claim 10 wherein the substrate is selected from fibers, woven or non-woven fabrics, carpets, leather and paper.

15

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 97/08140

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08G18/62 C08G18/28 C08G18/61 D06M15/576

According to International Patent Classification (IPC) or to both national classification and IPC:

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 185 421 A (COHEN GORDON M ET AL) 9 February 1993 see column 3, line 10 - column 4, line 61 see examples 5,6 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

*** Special categories of cited documents :**

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"E" earlier document but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

20 August 1997

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Van Puymbroeck, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCI/US 97/08140

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NONE